



# Selective catalytic reduction of NO with C1–C3 reductants over solvothermally prepared Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts: Effects of water vapor and hydrocarbon uptake

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## ABSTRACT

The influence of reducing agents (C1–C3 hydrocarbons) upon the selective catalytic reduction (SCR) of nitrogen oxide (NO) on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> solid solutions was explored. Under dry conditions, the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> solid solutions having large crystallite size had high activity for the SCR of NO with various hydrocarbons. However, under wet conditions, NO conversion on the catalyst decreased drastically for all the hydrocarbons. The decrease of NO conversion caused by the presence of water is due to the preferential adsorption of water which inhibits hydrocarbon adsorption on the catalyst surface. Among reductants of C1–C3 hydrocarbons, the most atom-efficient NO abatement was achieved with C2 hydrocarbons. C3 hydrocarbons were less selective for NO reduction than the other hydrocarbons. It was suggested that only one carbon atom per molecules were used for the SCR reaction, and the other carbon atoms were consumed by the simple combustion reaction.

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## 1. Introduction

Nitrogen oxide (NO) is one of the major air pollutants and causes the acid rain and ozone layer depletion. Besides severe environmental hazard, NO also has very harmful effects on the health of human beings. In recent years, a great deal of effort has been made for the removal of NO from the exhaust gases. The selective catalytic reduction (SCR) of NO is one of the most effective methods. In the large power plants, the SCR of NO with NH<sub>3</sub> on the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-based catalysts is used for the removal of NO<sub>x</sub> from the exhaust gases [1,2]. However, NH<sub>3</sub> is expensive and causes secondary pollution if NH<sub>3</sub> is leaked from the SCR device. On the other hand, the SCR with hydrocarbons (HC-SCR), especially methane, has many merits. Because hydrocarbons are less expensive than NH<sub>3</sub>, the cost performance of HC-SCR is much higher than that of NH<sub>3</sub>-SCR. Unreacted hydrocarbons can be easily removed by the catalytic combustion and complete conversion of NO<sub>x</sub> can therefore be attained by feeding excess hydrocarbons. Moreover, heat generated by combustion of hydrocarbons can be utilized easily especially for large scale power plants.

Shimizu et al. reported that the  $\gamma$ -alumina-supported gallium oxide (Ga<sub>2</sub>O<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) catalyst prepared by impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JRC ALO4) with a gallium nitrate solution showed high activities for CH<sub>4</sub>-SCR [3,4]. Haneda et al. prepared Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts by a sol-gel method and they reported that these catalysts exhibited high activities for C<sub>3</sub>H<sub>6</sub>-SCR [5].

We have been exploring the synthesis of inorganic materials in organic media at the temperatures higher than their boiling points (solvothermal method) [6]. Well-crystallized  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> solid solutions having high activities for CH<sub>4</sub>-SCR were directly obtained by a solvothermal method using diethylenetriamine as a solvent [7]. However, NO conversion over the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> solid solutions greatly decreased by the addition of water to the reaction gases [8]. The effect of water must be taken into consideration when the SCR catalysts are applied to the actual NO<sub>x</sub> removal process. There are a number of studies on the NO<sub>x</sub> removal under wet conditions [9–13]. Shimizu et al. reported that higher alkanes were effective for NO<sub>x</sub> removal over Ag/Al<sub>2</sub>O<sub>3</sub> catalysts in the absence [14] and presence of water [15]. For the Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst system, however, the effects of reductants have been scarcely explored. Shimizu et al. reported that C<sub>3</sub>H<sub>6</sub> was more effective reductants than CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> over Ga<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts [3]. Zahir et al. investigated HC-SCR with various reductants over ZnO–Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> ternary oxide catalysts. They

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found that the catalysts showed high NO conversion when  $C_3H_6$  was used as the reductant [16]. However, these reports examined the catalytic activity under dry conditions, and the effect of reductant on the catalytic performance under wet conditions has not been studied in detail. Moreover, some effects of water are surely revealed by comparing the catalytic performances of SCR with various reductants between dry and wet conditions. However, this point has not been discussed sufficiently in previous researches. From this aspect, we performed SCR of NO with various reductants under dry and wet conditions, and the adsorption of hydrocarbons on the  $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  catalyst under dry and wet conditions was also examined. Moreover, the relation between hydrocarbon uptake and NO conversions is discussed.

## 2. Experimental

### 2.1. Preparation of catalysts

The  $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  solid solutions were solvothermally prepared according to the method described previously [7]. In the typical synthesis, a mixture of gallium acetylacetonate (2.000 g) and aluminum triisopropoxide ( $\text{Al}(\text{O}^i\text{Pr})_3$ , 2.597 g,  $\text{Ga}/(\text{Ga} + \text{Al}) = 0.3$ ) was suspended in diethylenetriamine (80 ml) in a test tube, and the test tube was set in a 200-ml autoclave. Diethylenetriamine (30 ml) was added to the gap between the autoclave wall and the test tube. After the atmosphere of the autoclave was completely replaced with  $N_2$ , the autoclave was heated to 300 °C at the rate of 2.5 °C  $\text{min}^{-1}$ , kept at that temperature for 2 h, and allowed to cool to room temperature. White precipitates were collected, washed with acetone several times and air-dried. Catalysts were obtained by calcination of the products at 700 °C for 30 min.

### 2.2. Catalyst test

Catalyst tests for SCR of NO with various reductants were carried out in a fixed-bed flow reactor. The  $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  catalysts were pressed into pellets and crushed into 10–22 mesh, and 0.500 g of the catalyst was set in the quartz tube reactor. The catalyst bed was heated to 650 °C in a helium gas flow and held at that temperature for 30 min. Then, a reaction gas composed of NO (1000 ppm), a hydrocarbon (1000 ppm  $\text{CH}_4$ , 500–1000 ppm  $\text{C}_2\text{H}_6$  or  $\text{C}_2\text{H}_4$ , or 333–1000 ppm  $\text{C}_3\text{H}_8$  or  $\text{C}_3\text{H}_6$ ),  $\text{O}_2$  (6.7%),  $\text{H}_2\text{O}$  (0–10%) and helium balance was introduced to the reactor at  $W/F = 0.3 \text{ g s ml}^{-1}$  ( $SV \approx 11,000 \text{ h}^{-1}$ ). Reaction temperature was decreased from 650 to 250 °C at 50 °C intervals, and kept for 15 min to confirm the stationary state. The effluent gas was analyzed with an on-line gas chromatograph (CP2002, Chrompack, The Netherlands) every 5 min. A molecular sieve 5A column was used for analyzing oxygen, nitrogen, methane, and carbon monoxide, and a Porapak Q column, for carbon dioxide, ethane, propane, ethylene, and propylene. Conversions are defined in terms of NO conversion to  $N_2$  and hydrocarbon conversion to  $\text{CO}_2$  and CO.

Temperature-programmed desorption of hydrocarbons (HC-TPD) or NO (NO-TPD) was also carried out in the fixed-bed reactor.

The pretreatment condition was the same as that of the catalytic test (650 °C, 30 min in He). After the pretreatment in the helium flow, the catalyst bed was cooled to 100–250 °C in the same gas flow, and a gas mixture composed of a hydrocarbon (1000 ppm),  $\text{H}_2\text{O}$  (0 or 2.5%) and helium balance (for HC-TPD measurement), or of NO (1000 ppm),  $\text{O}_2$  (6.7%),  $\text{H}_2\text{O}$  (0 or 2.5%) and helium balance (for NO-TPD measurement) was introduced to the catalyst bed at  $W/F = 0.3 \text{ g s ml}^{-1}$  and kept flowing for 1 h. After excess hydrocarbon or NO was purged with a helium flow (100  $\text{ml min}^{-1}$ ) for 1 h, the temperature was raised to 700 °C at a rate of 5 °C  $\text{min}^{-1}$  in the same gas flow, and the effluent gas from the reactor was analyzed with a Pfeiffer Vacuum Omnistar GSD 301 O 1 quadrupole mass spectrometer.

## 3. Results and discussion

### 3.1. SCR of NO with various reductants

Well-crystallized  $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  solid solution was directly obtained by the solvothermal method [7,8]. The physical properties of the catalyst are summarized in Table 1.

Under the dry conditions, the catalyst was very effective for SCR of NO with C1–C3 alkanes and nearly 100% NO conversion was attained on the catalyst at  $T_{100}$  (the lowest temperature at which 100% HC conversion was attained), as shown in Fig. 1. However, when  $\text{H}_2\text{O}$  was added to the reaction gas, maximum NO conversions decreased to 50–80% and the peak temperature at which the catalyst showed the highest NO conversion was elevated.  $T_{100}$  became higher by the addition of  $\text{H}_2\text{O}$  to the reaction gas. Under wet conditions, the peak temperatures were 550 °C for  $\text{CH}_4$ -,  $\text{C}_2\text{H}_6$ -SCR, slightly lower than  $T_{100}$  for each reductant. However, over 75% HC conversion was attained at the peak temperature for  $\text{CH}_4$ -,  $\text{C}_2\text{H}_6$ -SCR. In the case of  $\text{C}_3\text{H}_8$ -SCR, the maximum NO conversion was obtained at  $T_{100}$  even under wet conditions. At the low temperature region (350–550 °C), both NO and hydrocarbon conversions decreased drastically. Therefore, water strongly inhibited active sites for both hydrocarbon [17] and NO [18] conversions at low temperatures.

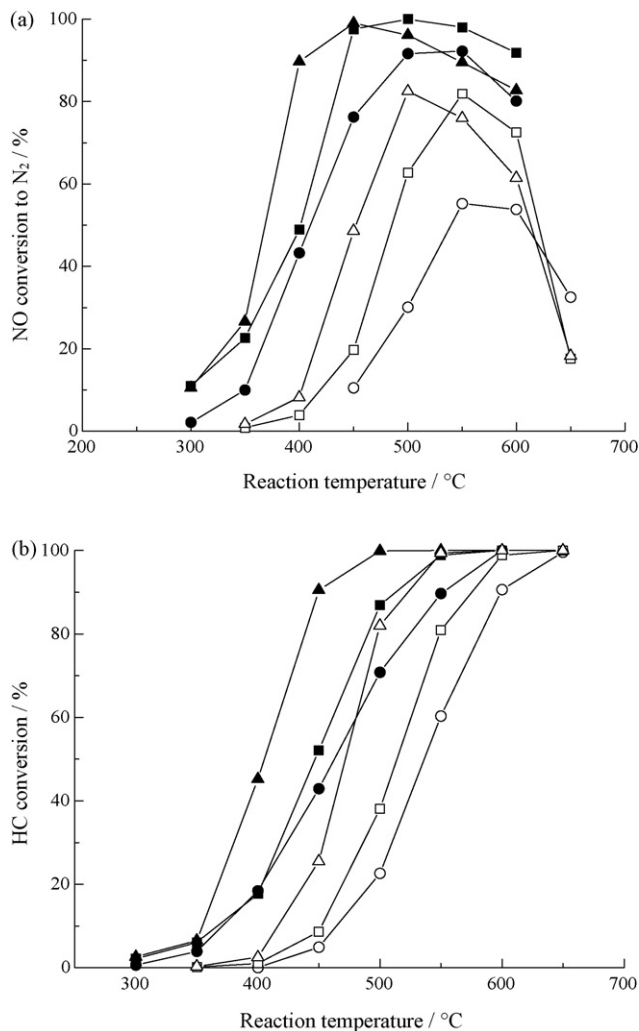
As shown in Fig. 2, the catalyst also showed high activity for SCR of NO with C2–C3 alkenes: NO conversions higher than 90% were attained in the absence of water. When propylene was used as the reductant, the catalyst turned pale brown during the reaction. However,  $\text{O}_2$  treatment of the used catalyst recovered the initial activity indicating that the color of the catalyst used for propylene-SCR was due to the formation of coke on the catalyst surface, the crystal structure being unaffected. Slightly lower NO conversion for  $\text{C}_3\text{H}_6$ -SCR than that for  $\text{C}_2\text{H}_4$ -SCR is presumably due to the coke formation.

When alkenes were used as the reductants, the catalyst exhibited higher activity even in the presence of water in the feed. In the case of  $\text{C}_3\text{H}_6$ -SCR, the peak temperature for SCR and  $T_{100}$  was not shifted by the presence of water. However, the NO conversion at relatively low temperatures decreased by the addition of  $\text{H}_2\text{O}$ .

**Table 1**  
Physical properties of  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  prepared by the solvothermal method

$\text{Ga}/(\text{Ga} + \text{Al})$		XRD		Surface area <sup>a</sup> ( $\text{m}^2 \text{g}^{-1}$ )	Crystallite size calculated from XRD <sup>a</sup> (nm)	Mode pore diameter <sup>a</sup> (nm)	Reference
Charged	Determined by		$\gamma$ -Type structure	151	10	12	[7]
	ICP	XPS					
0.30	0.29	0.21					

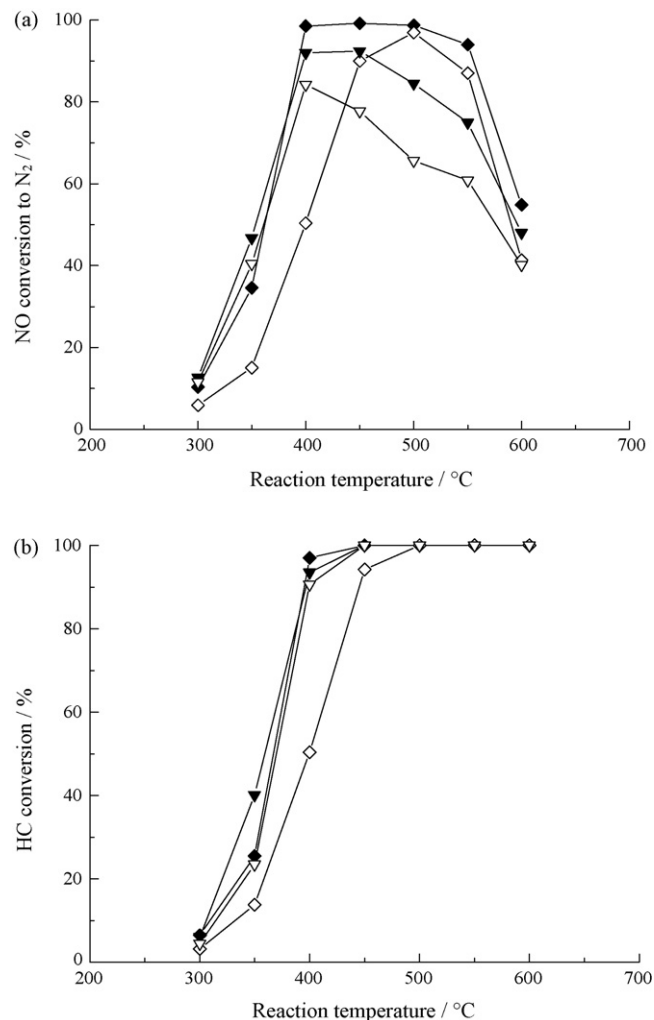
<sup>a</sup> Sample was calcined at 700 °C.



**Fig. 1.** NO (a) and alkane (b) conversions under dry (closed symbols) and wet (open symbols) conditions as a function of temperature. Reducing agent: (○, ●) methane; (□, ■) ethane; (△, ▲) propane. Reaction conditions: NO 1000 ppm; HC 1000 ppm; O<sub>2</sub> 6.7%; H<sub>2</sub>O 0% (closed symbols) or 2.5% (open symbols); He balance, W/F = 0.3 g s ml<sup>-1</sup>.

The results of catalytic test for dimethyl ether (DME)-SCR are shown in Fig. 3. The NO conversion was 40% at best, and the peak temperature was 400 °C. The catalysts showed the maximum NO conversion near  $T_{100}$  for DME, just as observed for HC-SCR. In DME-SCR, however, selectivity of the reductant used for NO reduction was low. Moreover, as shown in Fig. 4, the DME combustion proceeded much easily on the catalyst than the hydrocarbon combustion: for HC-SCR, especially SCR with alkanes, the conversion of NO was much higher than that of hydrocarbons in the lower temperature range. On the other hand, conversion of DME was much larger than conversion of NO, even at the low temperature range, suggesting that self-combustion of DME was more predominant reaction than the reaction with NO. Neither decrease in NO conversion nor shift of  $T_{100}$  occurred by the addition of water. These results show a sharp contrast against the results for HC-SCR. DME seems to have enough basicity to be adsorbed on the catalyst competing with the adsorption of water, and the details will be described in Section 3.2.

Fig. 4 shows the reactivity of various reductants for the catalytic combustion (i.e., in the absence of NO) under dry and wet conditions. Hydrocarbon conversion decreased drastically by the

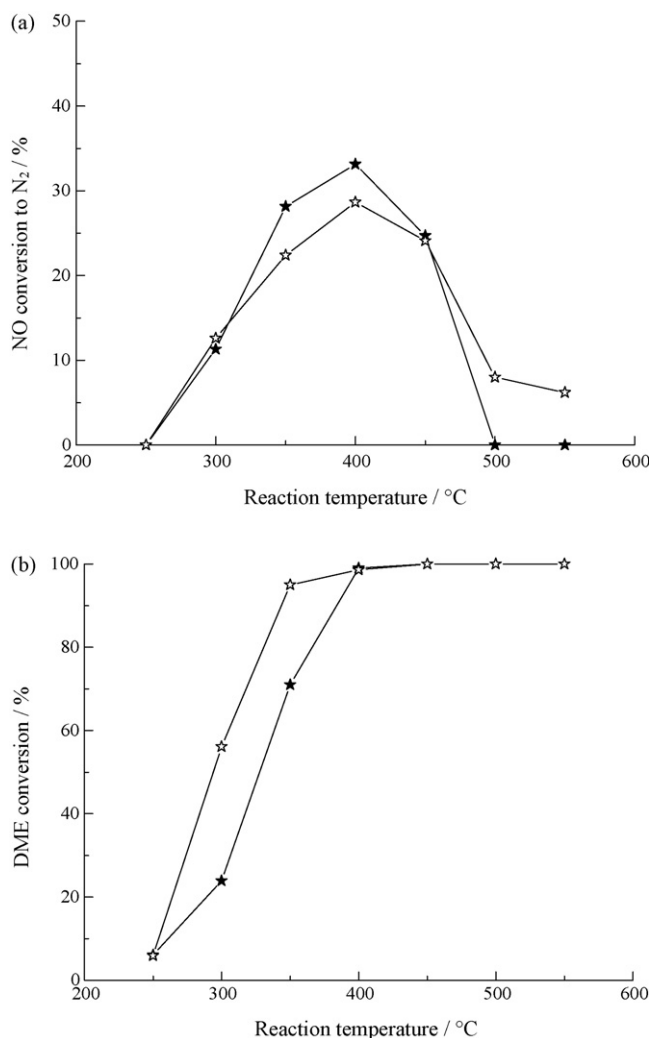


**Fig. 2.** NO (a) and alkene (b) conversions under dry (closed symbols) and wet (open symbols) conditions as a function of temperature. Reducing agent: (◇, ◆) ethylene; (▽, ▼) propylene. Reaction conditions: NO 1000 ppm; HC 1000 ppm; O<sub>2</sub> 6.7%; H<sub>2</sub>O 0% (closed symbols) or 2.5% (open symbols); He balance, W/F = 0.3 g s ml<sup>-1</sup>.

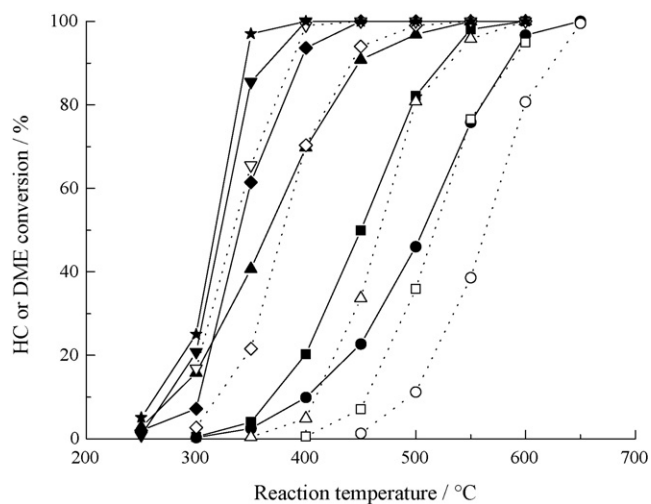
addition of water. This behavior was essentially identical with that found in HC-SCR reaction. These results suggest that the active sites for activation of hydrocarbon were strongly blocked by the water molecules in the reaction gases.

In Fig. 5, the ratio of the NO conversion under the wet conditions to that under dry conditions at 400 °C was plotted against the ratio of the hydrocarbon conversion in SCR under wet conditions to that under dry conditions at 400 °C for each hydrocarbon. A proportional relationship was observed indicating that the decrease of NO and hydrocarbon conversions caused by the presence of water was controlled by the same factor. In other words, the activation of hydrocarbons was inhibited by the water molecules adsorbed on the catalyst surface, which was directly related to the decrease in the catalytic activity for SCR of NO [19].

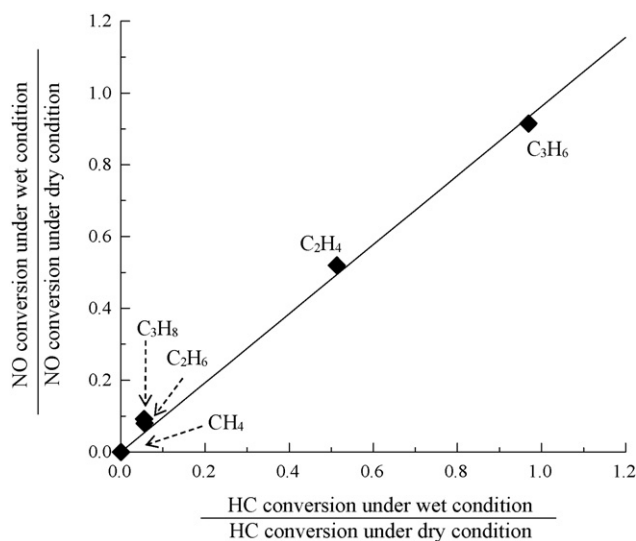
Fig. 6 shows the effect of water concentration in the feed gas upon the NO conversion. In HC-SCR, a small amount of water caused a drastic decrease in the NO conversion and further increase of water concentration resulted in only a slight decrease in the NO conversion. In the case of DME-SCR, on the other hand, NO conversion was not affected by the concentration of water.



**Fig. 3.** NO (a) and DME (b) conversions under dry (closed symbols) and wet (open symbols) conditions as a function of temperature. Reaction conditions: NO 1000 ppm; DME 1000 ppm; O<sub>2</sub> 6.7%; H<sub>2</sub>O 0% (closed symbols) or 2.5% (open symbols); He balance, W/F = 0.3 g s ml<sup>-1</sup>.



**Fig. 4.** Catalytic combustion test of hydrocarbons under dry (solid line) and wet (dotted line). (●) methane; (■) ethane; (▲) propane; (◆) ethylene; (▼) propylene; (★) DME. Reaction conditions: HC or DME 1000 ppm; O<sub>2</sub> 6.7%; H<sub>2</sub>O 0% (dry) or 2.5% (wet); He balance.



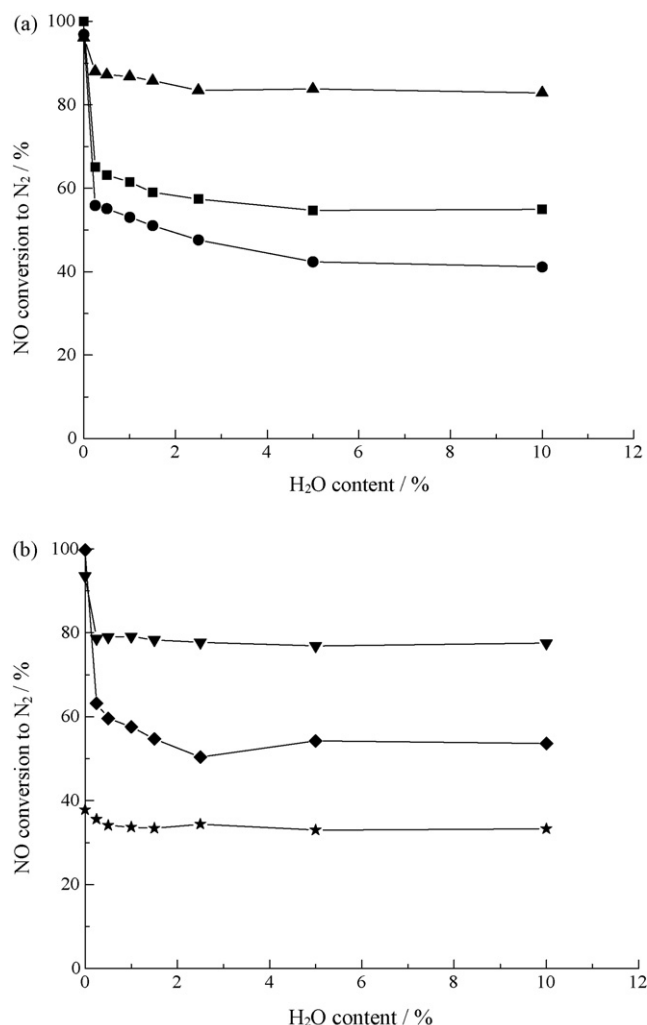
**Fig. 5.** Ratio of the NO conversion in the presence of water to those in the absence of water at 400 °C as a function of the ratio of the hydrocarbon conversion in the presence of water to that in the absence of water at 400 °C.

### 3.2. Hydrocarbon- and DME-TPD profiles

Fig. 7 shows the TPD profiles of methane, ethane, and propane preadsorbed at 250 °C on the catalyst. Under the dry conditions, large desorption peaks appeared at around 350 °C for three alkanes. When alkanes were introduced at 100 °C, no desorption peak appeared (data not shown) because physisorption of alkanes was very weak [20]. Dissociative adsorption of methane needs a large activation-energy [21]. Therefore, adsorption of alkanes occurred at high temperatures (~250 °C), and the peaks observed at ~350 °C are attributed to the desorption of chemisorbed alkanes. On the other hand, when alkanes were preadsorbed on the catalyst at 250 °C under the wet conditions, no desorption peaks appeared for methane and ethane, and a small desorption peak was seen for propane. These results suggest that water strongly inhibits the adsorption of alkanes on the catalyst surface.

Fig. 8 shows the TPD profiles of ethylene and propylene preadsorbed on the catalyst at 100 °C. Two desorption peaks were observed at ~150 and ~300 °C. The former peak is attributed to the desorption of alkenes chemisorbed with relatively weak force, and the latter to dissociatively adsorbed ones. The alkenes are strong electron-donors via their  $\pi$  electrons and adsorption through the  $\pi$  electrons possibly occurs. The desorption peak of propylene at ~150 °C was much larger than that of ethylene because propylene is a stronger electron-donor than ethylene. The adsorption occurred even under the wet conditions. However, water inhibited the dissociative adsorption of alkenes, thus lowering the catalytic activity. Despite the inhibiting effect of water, the desorption peaks due to the dissociative adsorption of alkenes appeared at the shoulder of the desorption peaks of weakly adsorbed alkenes. These adsorption behaviors were not observed in the case of alkanes.

The relationship between hydrocarbon conversion and hydrocarbon uptake due to the dissociative adsorption under dry and wet conditions is shown in Fig. 9. There is a tendency that when a larger amount of hydrocarbon is dissociatively adsorbed, the catalyst shows higher hydrocarbon conversion. However, the catalyst turned brown during the TPD measurements under the dry conditions, and H<sub>2</sub> ( $m/e = 2$ ) formation was observed except for CH<sub>4</sub>-TPD. These results suggest that coke was formed on the

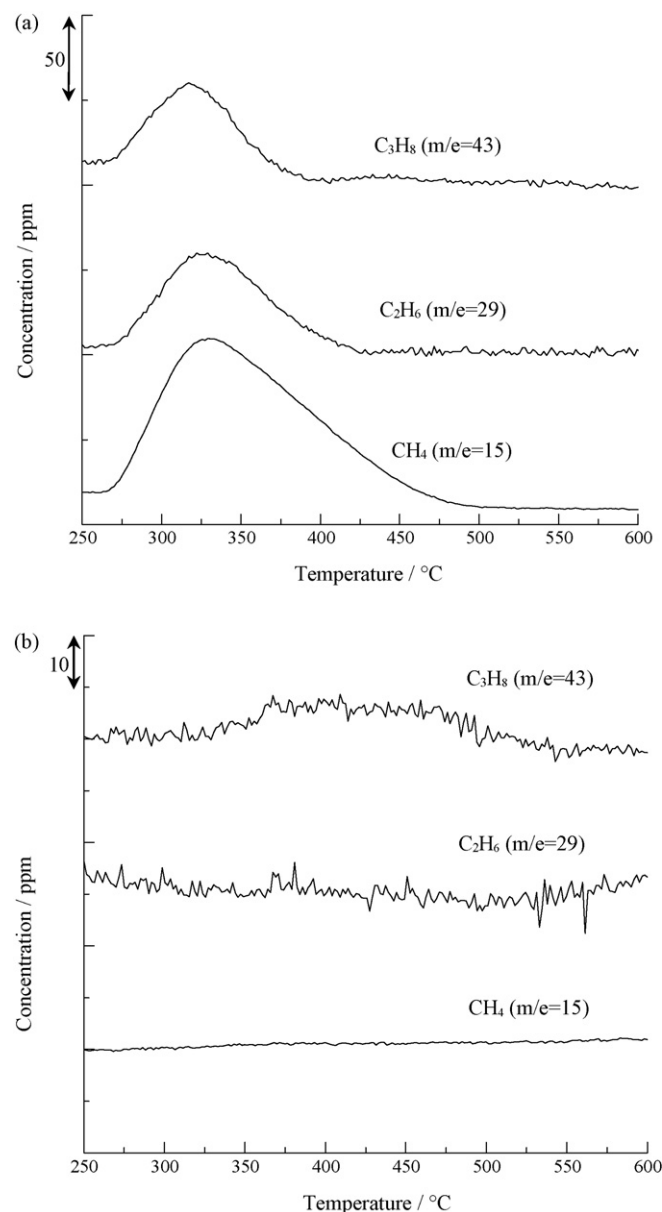


**Fig. 6.** NO conversion as a function of water content. Reducing agent: (a) (●) methane; (■) ethane; (▲) propane; (b) (★) DME; (◆) ethylene; (▼) propylene. Reaction conditions: NO 1000 ppm; HC or DME 1000 ppm; O<sub>2</sub> 6.7%; H<sub>2</sub>O 0–10%; He balance; reaction temperature; 400 °C (propylene, DME), 450 °C (ethylene), 500 °C (methane, ethane, propane).

catalyst during heating up to 700 °C in the He flow. Because of this effect, the hydrocarbon uptakes calculated from the TPD analysis were not so quantitative.

In Fig. 10, the ratio of the hydrocarbon conversion under the dry conditions to that under the wet conditions at 400 °C is plotted against the ratio of the dissociative hydrocarbon uptake of the catalyst under the wet conditions to that under the dry conditions. The decrease of the hydrocarbons uptake of the catalyst caused by the presence of water in the feed is the origin of the decrease of hydrocarbon conversion. In Section 3.1, it was shown that the decrease of NO conversion is in proportion to the decrease of hydrocarbon conversion. Therefore, the decrease of the amount of dissociatively adsorbed hydrocarbon causes the decrease of catalytic activity for SCR. Lowering the catalytic activity for CH<sub>4</sub>-SCR by water was largely due to the inhibitory effect of water upon the adsorption of methane on the catalyst surface.

For ion-exchanged zeolite system, the inhibitory effect of water is generally believed to be due to competitive adsorption of NO [22,23]. However, the crucial effect of water is different from catalyst to catalyst. For solvothermally prepared Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst, although NO uptake decreased about 70% by the addition

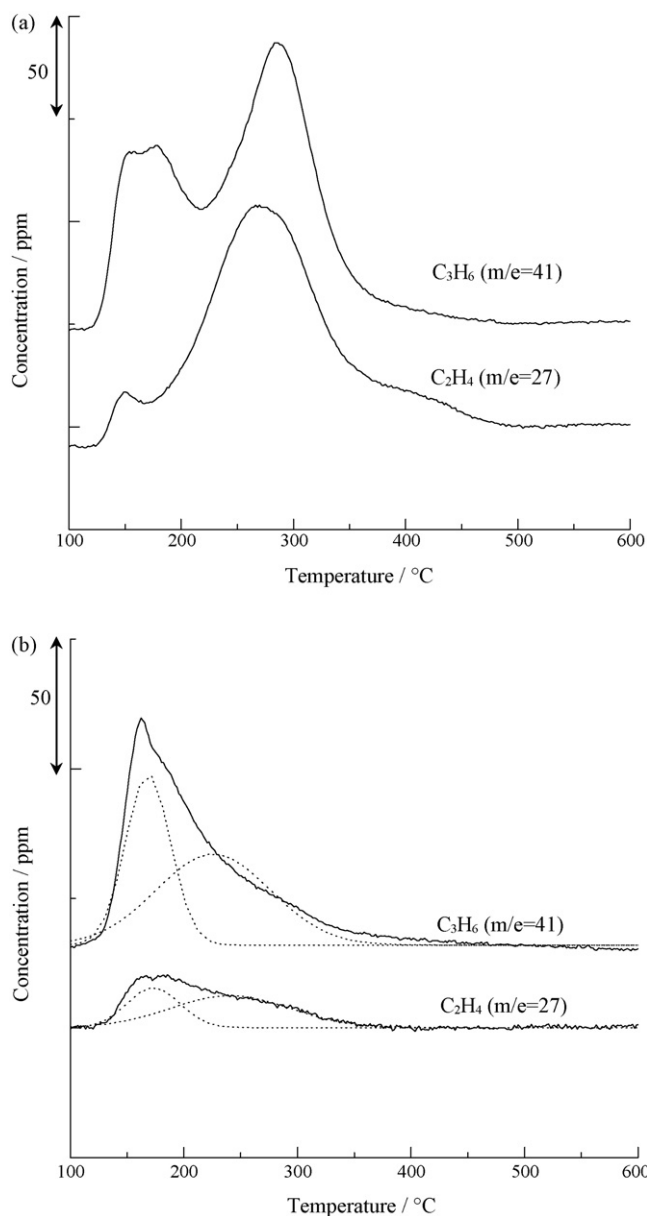


**Fig. 7.** TPD profiles of alkanes preadsorbed on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst under dry (a) and wet (b) conditions. Absorption conditions: 250 °C; HC 1000 ppm; H<sub>2</sub>O 0% (a) or 2.5% (b); He balance.

of water to the adsorption gas, a significant NO uptake was observed even under wet conditions (Fig. 11). The catalytic activity under wet conditions due to the inhibitory effect upon the adsorption of NO could not be disregarded. However, as shown in Fig. 10, the inhibitory effect of water upon the adsorption of hydrocarbons, especially lower alkanes like CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, was much larger than that upon the adsorption of NO. Therefore, it can be concluded that the dissociative adsorption of hydrocarbons (activation of hydrocarbons) seems to be the rate determining step for the hydrocarbon-SCR at low temperatures.

The DME-TPD profiles are shown in Fig. 12. The major fragments of the mass spectrum of DME itself are CH<sub>3</sub>OCH<sub>2</sub><sup>+</sup> (*m/e* = 45), CHO<sup>+</sup> (29), and CH<sub>3</sub><sup>+</sup> (15) [24]. In our mass spectrometer, the intensity of the *m/e* = 15 fragment was stronger than the other fragments. However, the *m/e* = 15 fragment was also detected when CH<sub>4</sub> was introduced. Therefore, we regarded the *m/e* = 45 fragment as the

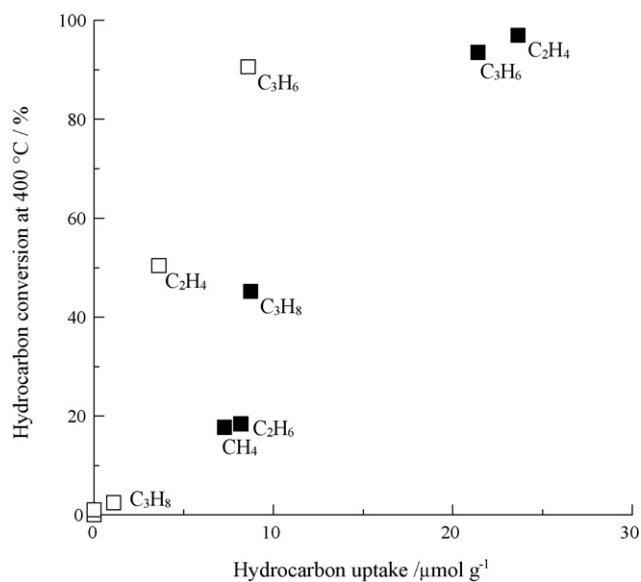




**Fig. 8.** TPD profiles of alkenes preadsorbed on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst under dry (a) and wet (b) conditions. Adsorption conditions: 100 °C; HC 1000 ppm; H<sub>2</sub>O 0% (a) or 2.5% (b); He balance.

evidence for desorption of DME during DME-TPD measurement. Fig. 12(a) shows that DME was not desorbed from the catalyst surface when DME was preadsorbed under the dry conditions. Instead, the broad desorption peaks of H<sub>2</sub> ( $m/e = 2$ ) and CO ( $m/e = 28$ ) were observed at around 350 °C, and sharp desorption peaks of CH<sub>4</sub> ( $m/e = 15$ ) and CO<sub>2</sub> ( $m/e = 44$ ) were also seen at around the same temperature range. These desorption peaks could not be attributed to the DME fragments, and these compounds described above were also detected by gas chromatography.

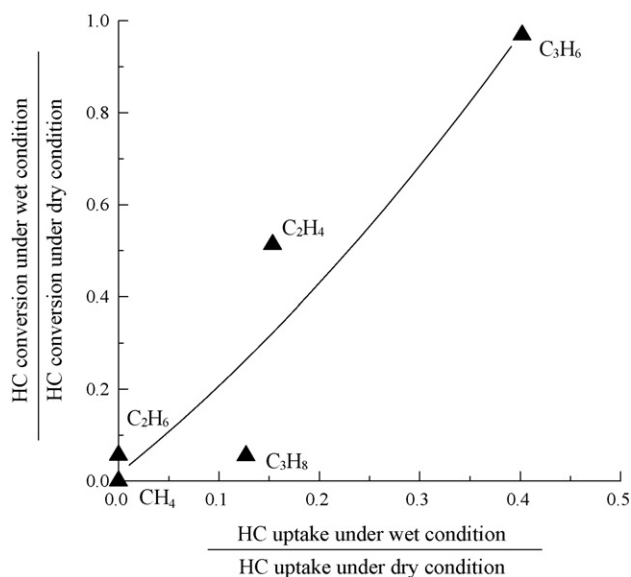
Previous DME-adsorption studies have shown that DME is adsorbed on  $\gamma$ -alumina surface as methoxy species [25] and it is well documented that methanol is also adsorbed as methoxy species. Moreover, surface methoxy groups were easily converted to H<sub>2</sub>, CH<sub>4</sub> and CO [26,27]. Therefore, it was concluded that DME was dissociatively adsorbed on the catalyst yielding surface methoxy groups, not only because the desorption peak of DME



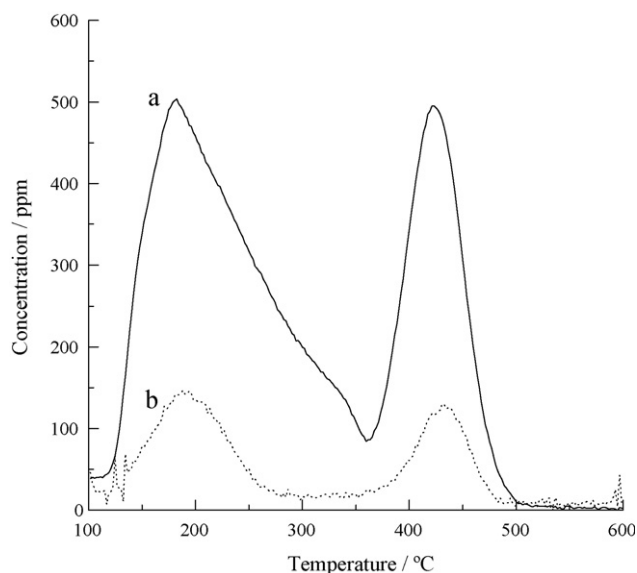
**Fig. 9.** Hydrocarbon conversion over the catalyst at 400 °C as a function of hydrocarbon uptake on the catalyst. Closed and open symbols correspond to the data under dry and wet conditions, respectively.

itself was not observed but also because formation of CO and H<sub>2</sub> were observed during the TPD analysis. Note that CO<sub>2</sub> was formed by the reaction of CO with the surface hydroxyl groups [28].

The desorption peak of DME itself, preadsorbed under the wet conditions was not observed either. However, the desorption peaks of H<sub>2</sub>, CO, and CO<sub>2</sub> were observed, which was the same behavior as observed under the dry conditions. These compounds were formed via surface methoxy groups as described above. On the other hand, CH<sub>4</sub> was not detected by mass spectrometric or gas chromatographic analysis. The difference in the desorbed compounds is attributed to the presence of the water adsorbed

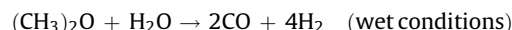
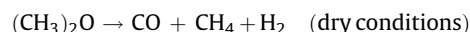


**Fig. 10.** Ratio of the hydrocarbon conversion in the presence of water to that in the absence of water at 400 °C as a function of the ratio of the amount of dissociatively adsorbed hydrocarbon in the presence of water to that in the absence of water. Reaction conditions were same as described in caption of Figs. 2 and 3. Adsorption conditions were same as Figs. 7 and 8.



**Fig. 11.** TPD profiles of NO preadsorbed on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst under dry (a) and wet (b) conditions. Adsorption conditions: 100 °C; NO 1000 ppm; O<sub>2</sub> 6.7%; H<sub>2</sub>O 0% (a) or 2.5% (b); He balance.

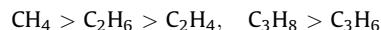
on the catalyst surface. A possible overall reaction for the DME decomposition is proposed as follows:



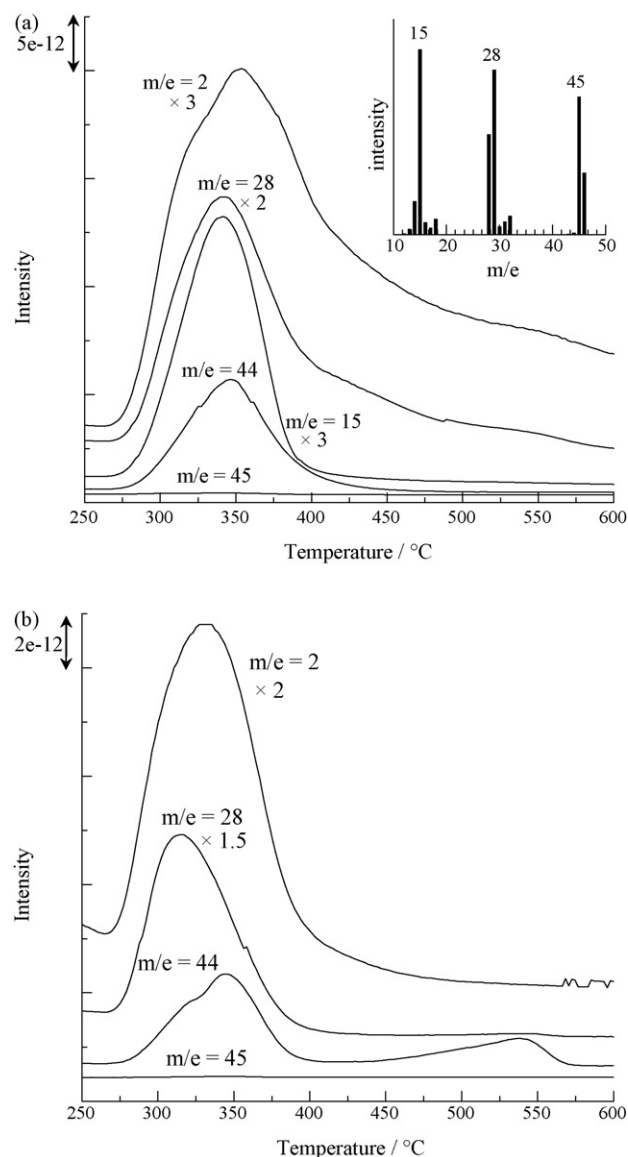
The TPD profile of DME preadsorbed under the wet conditions showed that chemisorption of DME was not inhibited by the addition of water in the feed. This effect explains the unique results of DME-SCR that NO conversion remained unchanged in the presence of water in the feed.

### 3.3. Effects of hydrocarbon concentration on the catalytic activity

Fig. 13 shows the catalytic tests for the reduction of NO with various hydrocarbons under the condition that the total concentration on carbon atoms was fixed to 1000 ppm. In the case of alkane-SCR, the temperature where the catalyst showed the maximum NO conversion was lowered with the increase of the carbon number in the reductant, and the same tendency was seen for alkene-SCR. The most effective temperature for the abatement of NO decreased according to the following order:

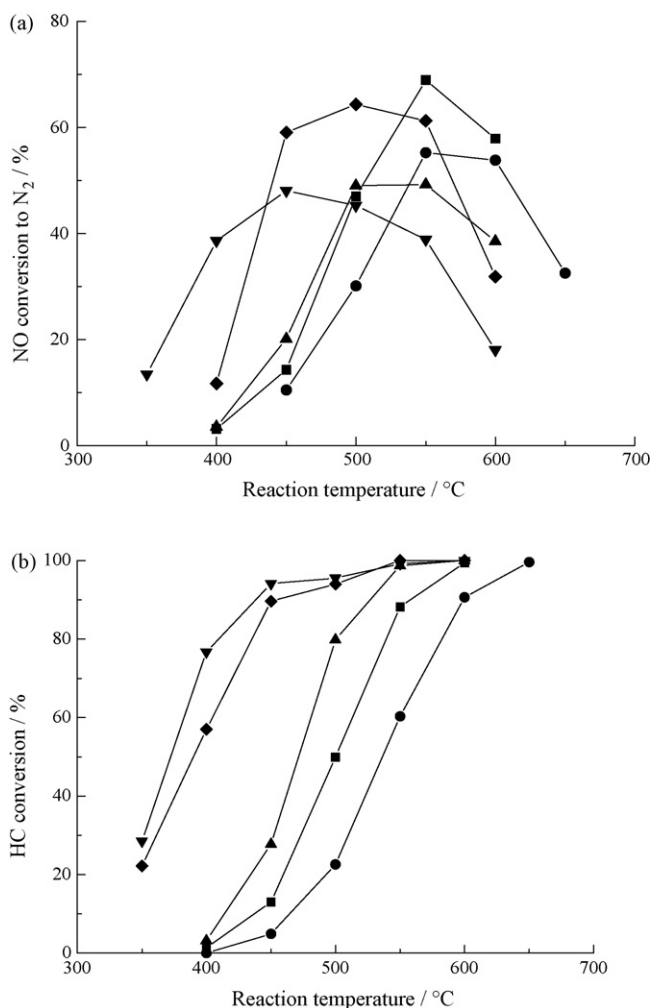


These results indicate that the activation of hydrocarbons occurs more easily with increasing the carbon number and that alkenes were activated more easily than alkanes. It is interesting to note that both ethane and ethylene gave approximately the same maximum NO conversions. Similar results were observed for propane and propylene. In other words, the maximum NO conversion is determined solely by the carbon number of the reductant whether the reductant is saturated or not. The maximum NO conversion of C3(C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>)-SCR was lower than that of C2(C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>)-SCR or CH<sub>4</sub>-SCR, although the catalyst showed almost the same hydrocarbon conversion (80–90%) at the temperature where the catalyst showed the maximum NO conversion. The carbon-based efficiency at the maximum NO conversion for HC-SCR decreases according to the following order: C2-SCR > CH<sub>4</sub>-SCR > C3-SCR



**Fig. 12.** TPD profiles of DME preadsorbed on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst under dry (a) and wet (b) conditions. Inset, mass spectrum of DME. Adsorption conditions: 250 °C; DME 1000 ppm; H<sub>2</sub>O 0% (a) or 2.5% (b); He balance.

The intermediate of the HC-SCR is presumed to be surface carboxylate species [29–31]. In the case of the C3 reductants, acetate species is formed predominantly, and acrylate or propionate was not detected as the reaction intermediate. The acetate species is also formed as an intermediate in C2-SCR. It was also reported that the surface carboxylate species and NO<sub>x</sub> species are converted into N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O via the isocyanate intermediate [14,30]. The result that the maximum NO conversion for C3-SCR was lower than that for C2-SCR on the basis of carbon efficiency indicates that C3 hydrocarbons was converted into the acetate species, which is accompanied by consuming a C1 fragment into CO<sub>2</sub> and H<sub>2</sub>O without being used for SCR reaction. This situation also occurs in the transformation of the acetate species into the isocyanate intermediate. When CH<sub>4</sub> is converted into a formate intermediate, no carbon fragment is consumed and one may therefore assume that CH<sub>4</sub> would be more atom-economically utilized in SCR. However, surface formate species is unstable [32] and easily decomposed into CO<sub>2</sub> and H<sub>2</sub>O without



**Fig. 13.** NO (a) and hydrocarbon (b) conversions under the conditions that the carbon-based concentration was fixed to 1000 ppm. (●) methane; (■) ethane; (▲) propane; (◆) ethylene; (▼) propylene. Reaction conditions: NO 1000 ppm; total amount of carbon atoms 1000 ppm; O<sub>2</sub> 6.7%; H<sub>2</sub>O 2.5%; He balance.

reacting with NO<sub>x</sub> species. Therefore, the maximum NO conversion for CH<sub>4</sub>-SCR was lower than C2-SCR.

#### 4. Conclusions

Under the dry conditions, well-crystallized  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> solid solution prepared by the solvothermal method showed very high activity for the SCR of NO with C1–C3 hydrocarbons. Except for CH<sub>4</sub>, more than 80% of NO conversion was attained even under the wet conditions.

On the basis of the carbon efficiency, C2 hydrocarbons were the most effective for SCR of NO, and C3 hydrocarbons were less effective than any other hydrocarbons examined in the present study.

Under the dry conditions, the dissociative adsorption of hydrocarbons on the catalyst surface was closely related to hydrocarbon conversion. The presence of water greatly decreased the amounts of adsorbed hydrocarbons and NO on the catalyst resulting in a decrease of NO conversion. However, the crucial effect of water was competitive adsorption with hydrocarbons on the catalyst surface.

The catalyst showed poor activity for the DME-SCR. However, NO conversion was almost unchanged even in the presence of water. These results were explained by the fact that the water scarcely had the inhibitory effect for the dissociative adsorption of DME.

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